Key analytical techniques for all four carbonate chemistry parameter measurements: challenges, Limitations, and misconceptions

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WHAT DO WE MEAN BY *CARBONATE CHEMISTRY PARAMETERS*?

Items of information needed to characterize the CO_2 system in a seawater sample:

1. Measurements made on the seawater sample
   e.g., pH, total dissolved inorganic carbon, . . .
2. Information such as equilibrium constants, *etc.* inferred from measured *S*, *T*, *&* *p* of the sample
   e.g., CO_2 dissociation constants, total boron, . . .
3. Information calculated from 1 and 2
   e.g., $p(CO_2)$, aragonite saturation state, . . .

HOW MIGHT YOU GO ABOUT SPECIFYING *MEASUREMENT REQUIREMENTS*?

Ask yourself three questions:

1. What carbonate parameters do I need to know?
2. How well do I need to know them?
3. What resources do I need to achieve this?

These, of course, may be specified for you.

HOW MIGHT THESE CHANGE FOR *DIFFERENT ECOSYSTEMS AND APPLICATIONS*?

How will the requirements change?

1. Are different parameters required?
2. Are there different requirements for measurement uncertainty?
3. Will this have implications for the resources needed?

FROM THE POINT OF VIEW OF THE ANALYST, TWO KEY QUESTIONS ARISE FOR A MEASUREMENT:

1. How good is the measurement?
2. How good is good enough?

Need to provide an estimate of the measurement uncertainty , that can be compared against a specified target uncertainty.

Note, measurement uncertainty is not the same as precision!

MEASUREMENT UNCERTAINTY

A non-negative parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

NOTE 1: This parameter is usually expressed as the half-width of an interval having a stated coverage probability.

NOTE 2: Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

PRECISION

Closeness of agreement between independent test results obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results. Less precision is reflected by a larger standard deviation.

NOTE 3 “Independent test results” means results obtained in a manner not influenced by any previous result on the same or similar test object. Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

WHAT IS QUALITY?

Quality is fitness for purpose.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Fitness for purpose therefore refers to the magnitude of the uncertainty associated with a measurement in relation to the needs of the application area.

Has implications for the level of resources needed!

MEASURED SEAWATER CARBON PARAMETERS

On occasion $[\mathrm{CO}_3^{2-}]$ is estimated from its effect on the spectrum of lead in seawater

USUAL PARAMETERS MEASURED

- Total dissolved inorganic carbon

$$C_\mathrm{T} = [\mathrm{CO}_2] + [\mathrm{HCO}_3^-] + [\mathrm{CO}_3^{2-}]$$

- Total hydrogen ion concentration (pH)

$$\mathrm{pH} = -\lg\,[\mathrm{H}^+]$$

- Partial pressure of CO_2 (in air in equilibrium with sea water)

$$p(\mathrm{CO}_2) = x(\mathrm{CO}_2)\,p = [\mathrm{CO}_2]/K_0$$

- Total alkalinity

$$A_\mathrm{T} = [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{B(OH)}_4^-] + [\mathrm{OH}^-] - [\mathrm{H}^+]$$

	Advantages	Disadvantages
C_T	T, p independent Unambiguous interpretation of changes	Needs care with sample handling No autonomous system available
pH	Autonomous systems available Master variable?	Function of T, p Needs care with sample handling Interpretation problems
$p(CO_2)$	Autonomous systems available	Function of T, p Changes not easy to interpret
A_T	T, p independent Often possible to interpret changes	No autonomous system available Harder to interpret in some systems

TOTAL DISSOLVED INORGANIC CARBON

- Carbon dioxide mass balance equation

$$C_\mathrm{T} = [\mathrm{CO_2}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]$$

T, p independent

UNITS: moles per kilogram of solution (usually μmol $\mathrm{kg^{-1}}$)

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1. Acidify a known amount of sample
2. Extract the $\mathrm{CO_2}$
3. Measure the amount of $\mathrm{CO_2}$ extracted
    - Coulometry
    - Infra-red analyzer
    - Manometry
    - Other

COMPARISON OF TECHNIQUES

	Advantages	Disadvantages
IR system	Cheaper system Faster sample throughput Less waste disposal Less *start-up* time Smaller sample ?	Lower reproducibility Calibration not v. stable Limited collaborative testing as yet
Coulometry system	Higher reproducibility Stable calibration Well tested in many labs	Slower sample throughput Proprietary coulometer solution (hazardous) Significant *start-up* time needed

TOTAL HYDROGEN ION CONCENTRATION (PH)

- Species concentration, $[H^+]$

$$\mathrm{pH} = -\lg\,[\mathrm{H}^+]$$

T, p dependent

UNITS: pH is dimensionless
But, total hydrogen ion concentration is in moles per kilogram of solution

TOTAL HYDROGEN ION CONCENTRATION (PH)

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$$\mathrm{pH} = -\lg\,[H^+]$$

T, p dependent

UNITS: pH is dimensionless
But, total hydrogen ion concentration is in moles per kilogram of solution

1. Electrometric measurement of pH
2. Spectrophotometric measurement of pH

ELECTROMETRIC PH MEASUREMENT

A direct electrometric technique using an electrode sensitive to hydrogen ion in a "pH cell";

The Nernst equation underlies this approach to measuring pH:

$$E = E^*(S, T, p) - \left(\frac{RT\ln 10}{F}\right)\lg[\mathrm{H}^+]$$

$$= E^*(S, T, p) + \left(\frac{RT\ln 10}{F}\right)\mathrm{pH}$$

$$\mathrm{pH(X)} = \mathrm{pH(S)} - \frac{E_\mathrm{X} - E_\mathrm{S}}{RT\ln 10 / F}$$

For this operational approach to give an accurate estimate of $[\mathrm{H}^+]$, it is essential that the calibration standard be matched closely to the sample in composition.

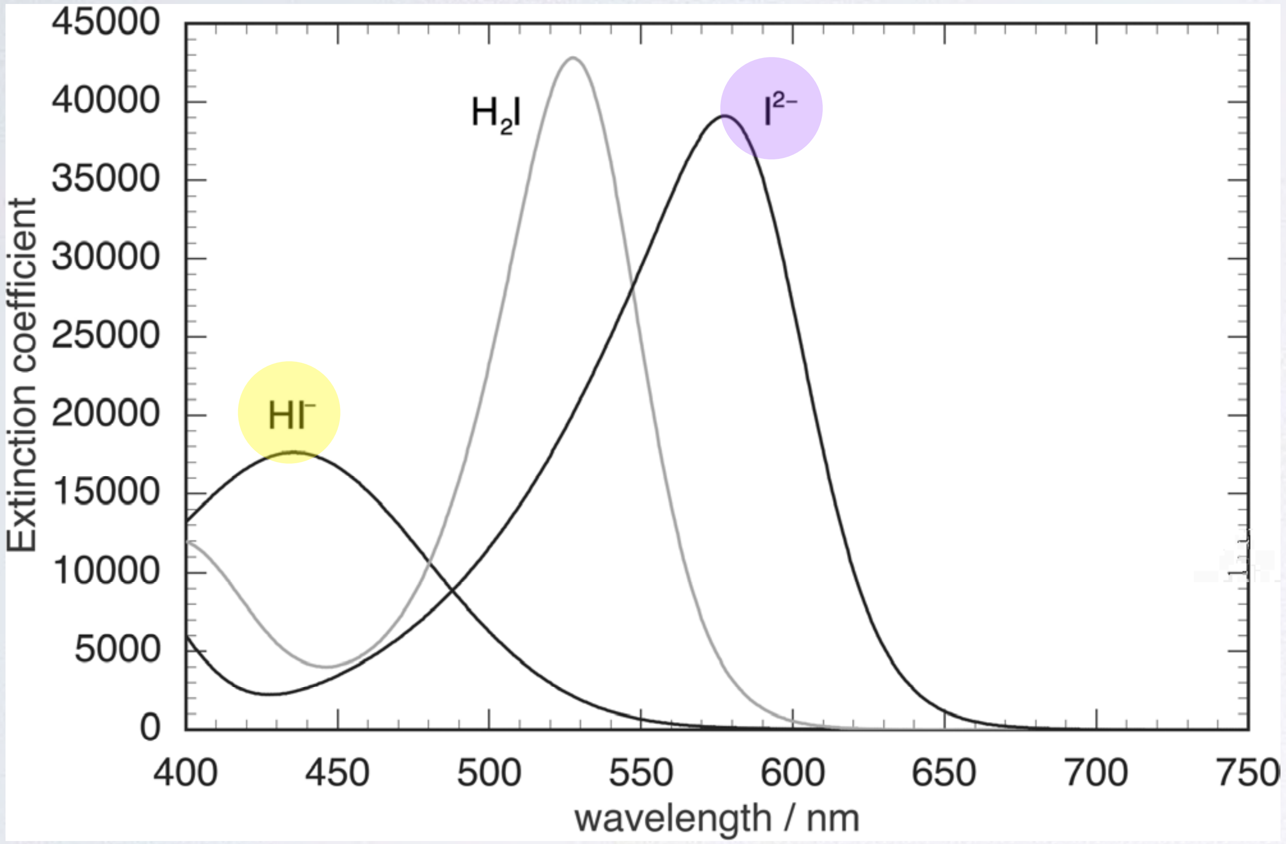
IT RARELY IS !

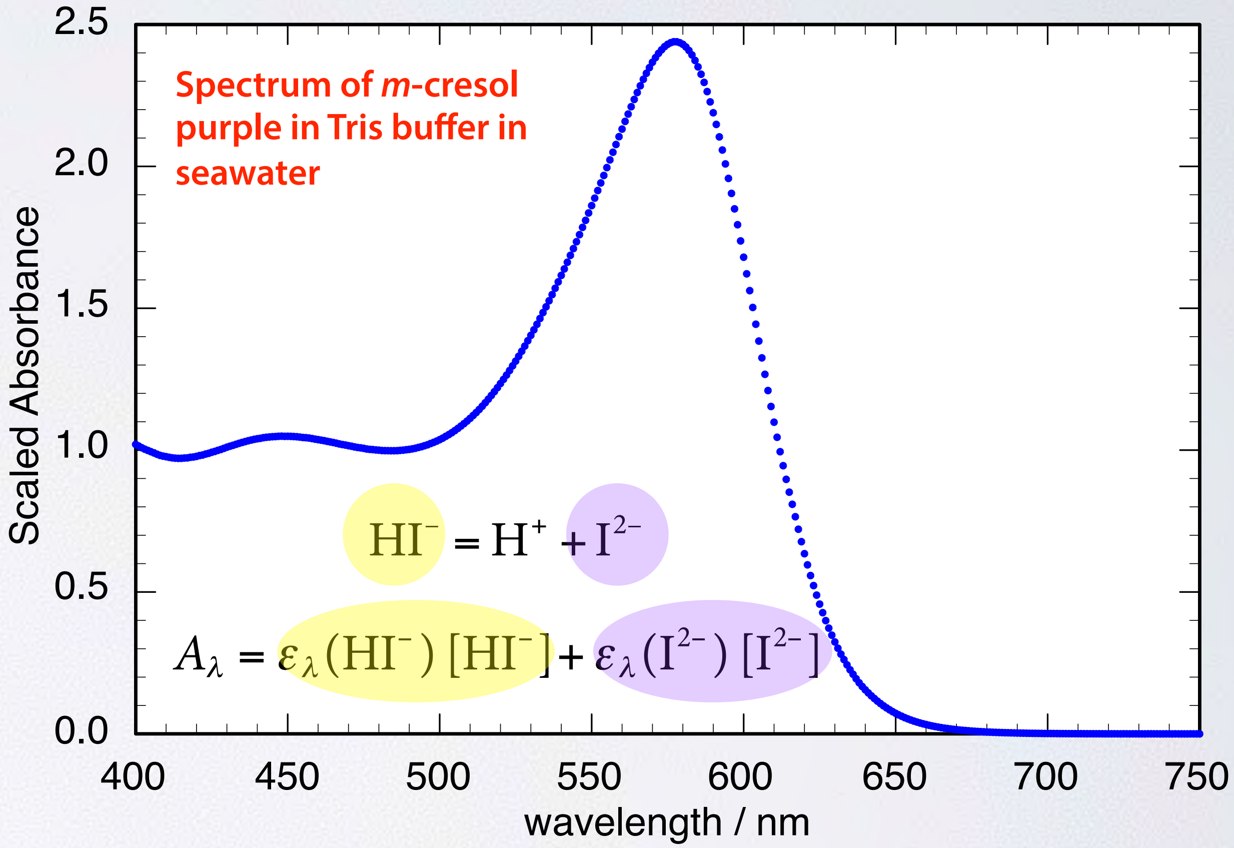
To use autonomously (not constant S, T, p), it is essential that the functional form of $E^*(S, T, p)$ be known well.

IT OFTEN ISN'T!

Spectrophotometric pH measurement

A colorimetric technique in which an indicator dye is added to the solution and the pH inferred from the resulting absorbance spectrum (color).





Spectrum of *m*-cresol purple in Tris buffer in seawater

$$HI^- = H^+ + I^{2-}$$

$$A_\lambda = \varepsilon_\lambda(HI^-)\,[HI^-] + \varepsilon_\lambda(I^{2-})\,[I^{2-}]$$

$$\mathrm{pH} = -\lg K(\mathrm{HI}^-)\left(\frac{\varepsilon_1(\mathrm{I}^{2-})}{\varepsilon_2(\mathrm{HI}^-)}\right) + \lg\left(\frac{A_1/A_2 - \varepsilon_1(\mathrm{HI}^-)/\varepsilon_2(\mathrm{HI}^-)}{1-(A_1/A_2)\varepsilon_2(\mathrm{I}^{2-})/\varepsilon_1(\mathrm{I}^{2-})}\right)$$

POTENTIAL IMPLICATIONS OF USING IMPURE DYE

Environmental Science & Technology

ARTICLE

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Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements

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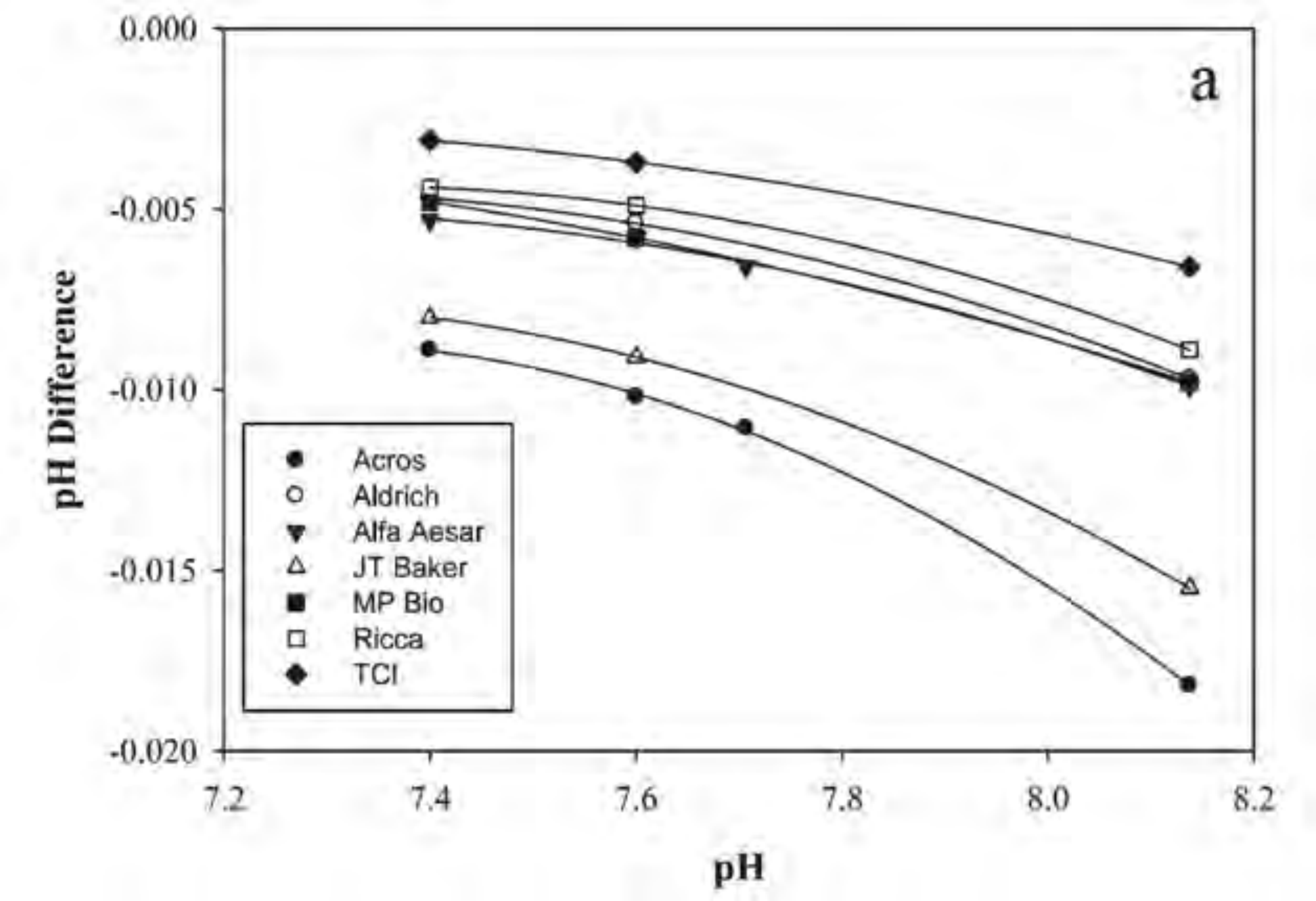
, 140 Seventh Avenue South, St. Petersburg, Florida 33701, United States

pid and precise measurements
acid–base indicators used in
ccuracy. This work describes
eta-cresol purple (mCP), and
modynamic equilibrium con-
perature (T) and salinity (S).
on concentration scale (pH_T)
nce ratios ($R = {}_{\lambda_2}A/{}_{\lambda_1}A$) as



Thus far the uncertainty introduced by dye impurities has only been characterized at a single temperature (25 °C) and salinity (35).

COMPARISON OF TECHNIQUES

	Equipment Cost (need *T* control)	Ease of use	Uncertainty in best labs
Electrometric pH cell	Relatively cheap	Simple to use, needs regular recalibration*	0.02 limited availability of RMs
Using indicator & spectrophotometer	Mid-range k$ 10–25	Can be automated	< 0.01 limited availability of pure mCP

- ✶ The Honeywell DuraFET® seems to have a significantly more stable calibration than a conventional pH cell.

PARTIAL PRESSURE OF CO_2

(IN AIR THAT IS IN EQUILIBRIUM WITH THE WATER SAMPLE)

- Species concentration, $[CO_2]$

$$\mathrm{CO_2(g) = CO_2(aq)} \qquad K_0(T, p, S) = \frac{[\mathrm{CO_2}]}{\underbrace{x(\mathrm{CO_2})}_{\text{mole fraction of } \mathrm{CO_2}} \cdot \underbrace{p}_{\text{equilibration pressure}}}$$

$$p(\mathrm{CO_2}) = x(\mathrm{CO_2})\, p = [\mathrm{CO_2}] / K_0$$

T, p dependent

UNITS: pressure units (usually μatm)

PARTIAL PRESSURE OF CO_2
(IN AIR THAT IS IN EQUILIBRIUM WITH THE WATER SAMPLE)

- Species concentration, $[CO_2]$

$$p(CO_2) = x(CO_2)\,p = [CO_2]/K_0$$

T, p dependent

A. Gas phase equilibration
   - Measure $x(CO_2)$ in the gas phase using NDIR
   - Measure $x(CO_2)$ in the gas phase using GC

B. Membrane equilibration (with gas or external solution)
   - Measure $x(CO_2)$ in the gas phase using NDIR
   - Measure pH in external solution (*see pH section*)

COMPARISON OF TECHNIQUES

	Equipment Cost	Advantages / Disadvantages	Uncertainty*
infra-red analyzer	\$30,000 – \$60,000	Quality depends mostly on design of equilibrator	With careful calibration < 0.5%
pH-based analyzer	~\$25,000	Awkward to calibrate Membrane can foul	Can be 1–2%

* These values are for commercial systems when working well.

TOTAL ALKALINITY

$$A_\mathrm{T} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}]$$

T, p independent

UNITS: moles per kilogram of solution (usually μmol $\mathrm{kg^{-1}}$)

TOTAL ALKALINITY

- Hydrogen ion mass-balance equation

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$ *T, p independent*

Acidimetric titration

- Closed-cell
- Open-cell

a. Can also add acid in one aliquot (single point method)

b. Can use either a pH cell or spectrophotometry to estimate $[H^+]$ during titration.

c. Ideally use NLLS to locate equivalence point;
can use Gran technique

COMPARISON OF TECHNIQUES

	Equipment Cost	Advantages / Disadvantages	Uncertainty*
Closed cell	~\$30,000	Uses cell to measure *V* Problems with back-pressure	~2-4 μmol kg^{-1}
Open cell	\$15,000 to \$30,000	Can be very precise Easier to diagnose faults	~1–4 μmol kg^{-1}

* These values are for commercial systems when working well.

STATUS OF CURRENT MEASUREMENT PRACTICE

SAMPLING & ANALYSIS STRATEGIES

Discrete samples (collected from desired locations, preserved, then analyzed later in a laboratory)

Automated on-line analysis (*e.g.* a stream of sea water pumped into the instrument)

Instruments operated in a profiling mode, *e.g.* as part of a CTD package

Autonomous instruments able to carry out their analyses remotely in the ocean

DEVELOPMENT STATE OF CO_2 MEASUREMENT SYSTEMS

Level 0 – No working system available

Level 1 – Prototype system available in single lab

Level 2 – 2nd generation prototype in use

Level 3 – Home-built systems in a number of labs

Level 4 – Can be purchased commercially

Level 5 – Commercially available, reliable, and fully supported

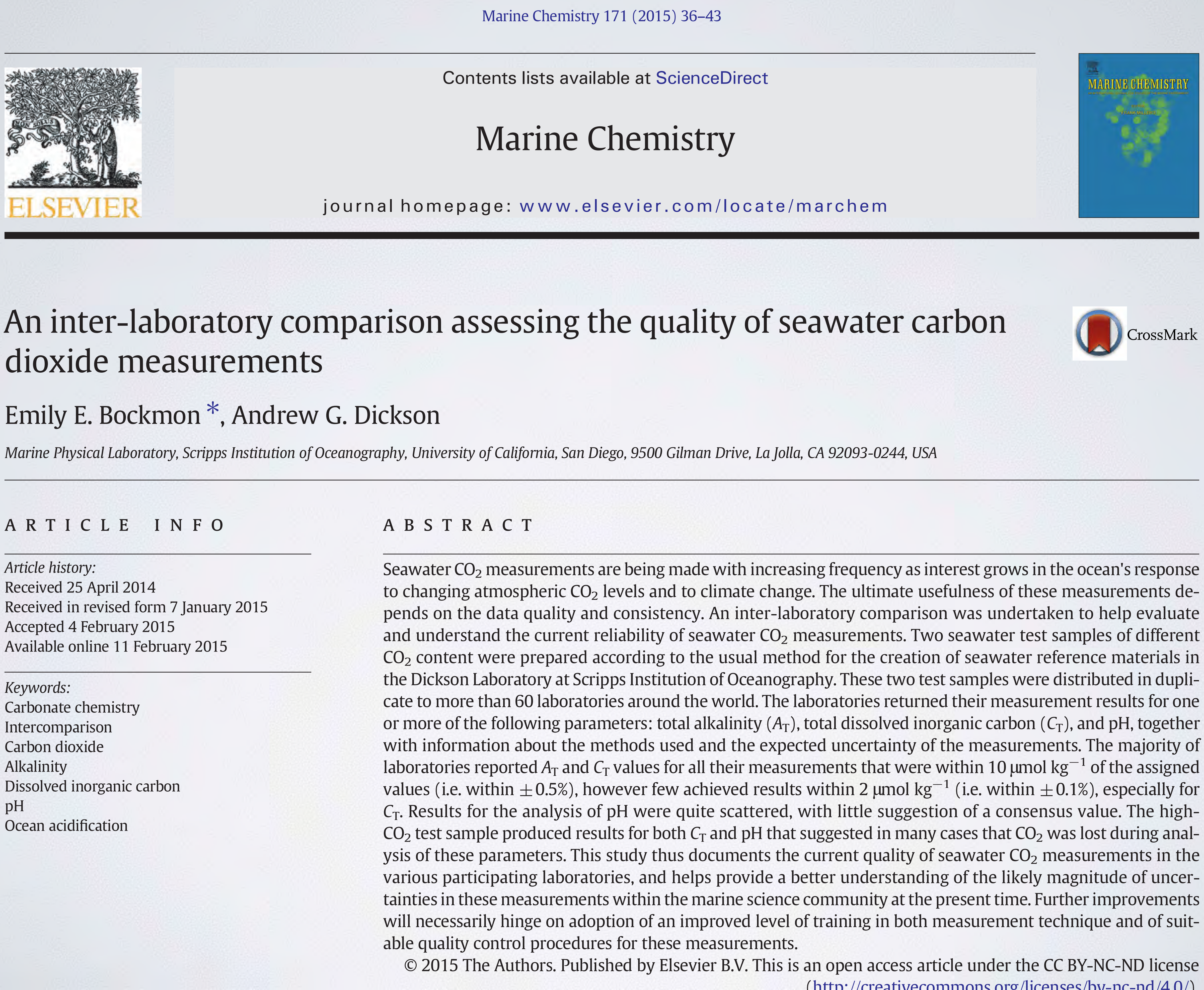
DEVELOPMENT STATE OF CO_2 MEASUREMENT SYSTEMS

	Discrete samples	Autonomous sampling & analysis	Profiling instrument	Remote instruments in ocean
C_T	3/4/5?	1/2	0	0/1
pH	3/4	3/4/5?	1/2	3/4/5?
$p(CO_2)$	2	3/4/5	1	3/4/5
A_T	3/4/5?	1/4	0	0/1

ESTIMATED UNCERTAINTIES† FOR DISCRETE MEASUREMENTS

	State-of-the-art laboratory	State-of-the-art at-sea lab (suitable RMs)	Other laboratories (suitable RMs)	Laboratories not using RMs
C_T	1.0 µmol kg⁻¹	2 µmol kg⁻¹	4–10 µmol kg⁻¹	?
pH	0.010 (0.004 ?)	0.010 (0.004 ?)	0.01–0.05	?
$p(CO_2)$ IR-based	1.0 µatm	2 µatm	5–10 µatm	?
A_T	1.2 µmol kg⁻¹	2 µmol kg⁻¹	4–10 µmol kg⁻¹	?

† Based on measuring surface oceanic CO_2 levels



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An inter-laboratory comparison assessing the quality of seawater carbon dioxide measurements

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ABSTRACT

Seawater CO_2 measurements are being made with increasing frequency as interest grows in the ocean's response to changing atmospheric CO_2 levels and to climate change. The ultimate usefulness of these measurements depends on the data quality and consistency. An inter-laboratory comparison was undertaken to help evaluate and understand the current reliability of seawater CO_2 measurements. Two seawater test samples of different CO_2 content were prepared according to the usual method for the creation of seawater reference materials in the Dickson Laboratory at Scripps Institution of Oceanography. These two test samples were distributed in duplicate to more than 60 laboratories around the world. The laboratories returned their measurement results for one or more of the following parameters: total alkalinity (A_T), total dissolved inorganic carbon (C_T), and pH, together with information about the methods used and the expected uncertainty of the measurements. The majority of laboratories reported A_T and C_T values for all their measurements that were within 10 μmol kg^{-1} of the assigned values (i.e. within ±0.5%), however few achieved results within 2 μmol kg^{-1} (i.e. within ±0.1%), especially for C_T. Results for the analysis of pH were quite scattered, with little suggestion of a consensus value. The high-CO_2 test sample produced results for both C_T and pH that suggested in many cases that CO_2 was lost during analysis of these parameters. This study thus documents the current quality of seawater CO_2 measurements in the various participating laboratories, and helps provide a better understanding of the likely magnitude of uncertainties in these measurements within the marine science community at the present time. Further improvements will necessarily hinge on adoption of an improved level of training in both measurement technique and of suitable quality control procedures for these measurements.

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RECENT INTER-LABORATORY PROFICIENCY STUDY

Assigned values for total alkalinity, total dissolved inorganic carbon, and pH (25 °C; total scale) for the two test samples. Values are expressed as *mean ± standard deviation* (*number of analyses*).

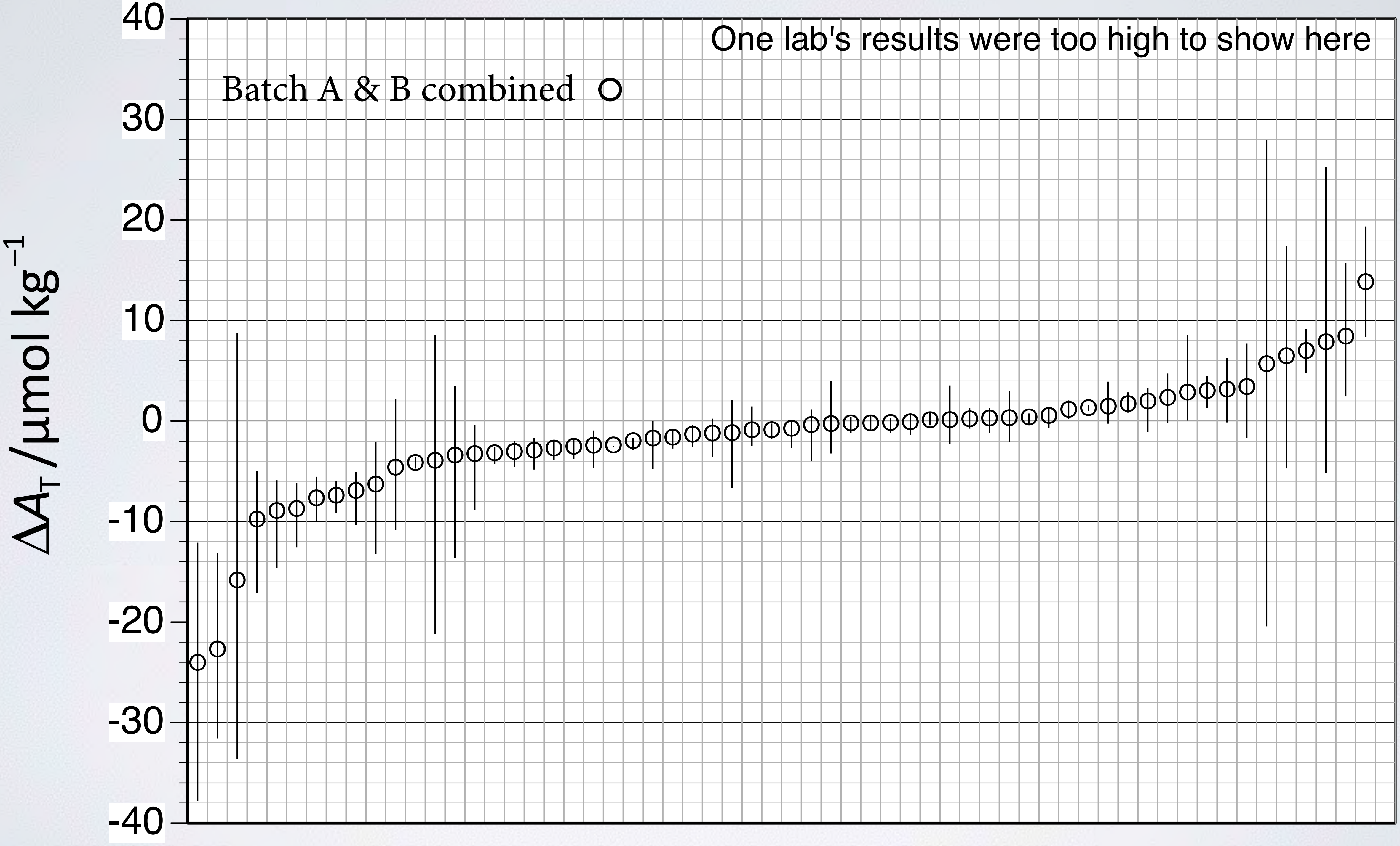
	Batch A	**Batch B**
Salinity	33.190	33.186
Total alkalinity	2215.08 ± 0.49 (24) μmol kg^{-1}	2216.26 ± 0.52 (18) μmol kg^{-1}
Total dissolved inorganic carbon	2015.72 ± 0.74 (9) μmol kg^{-1}	2141.94 ± 0.37 (6) μmol kg^{-1}
pH (25 °C; total scale)	7.8796 ± 0.0019 (18)	7.5541 ± 0.0020 (18)

Normal RM

High-CO_2 RM

Bockmon & Dickson, 2015

RECENT INTER-LABORATORY PROFICIENCY STUDY



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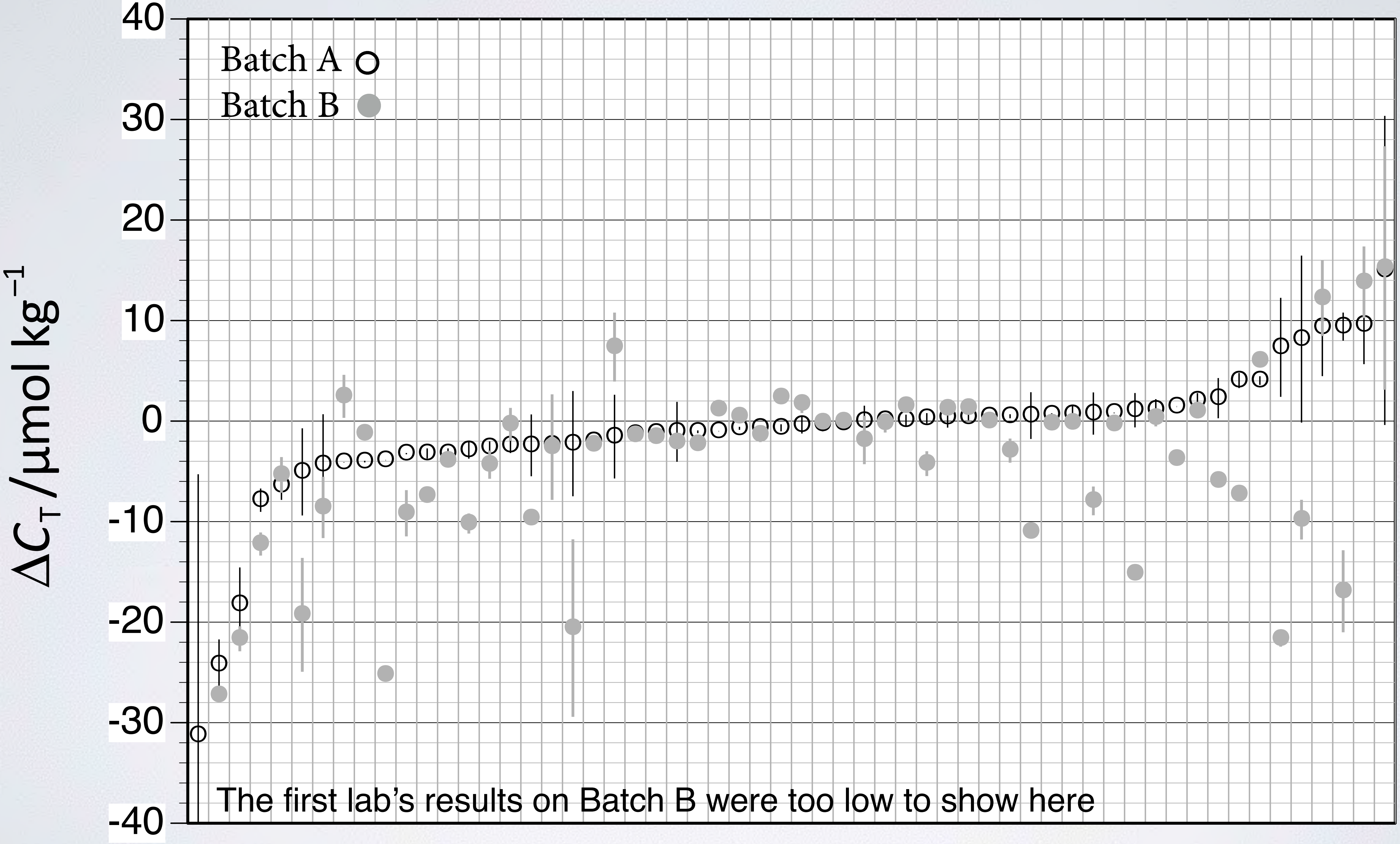

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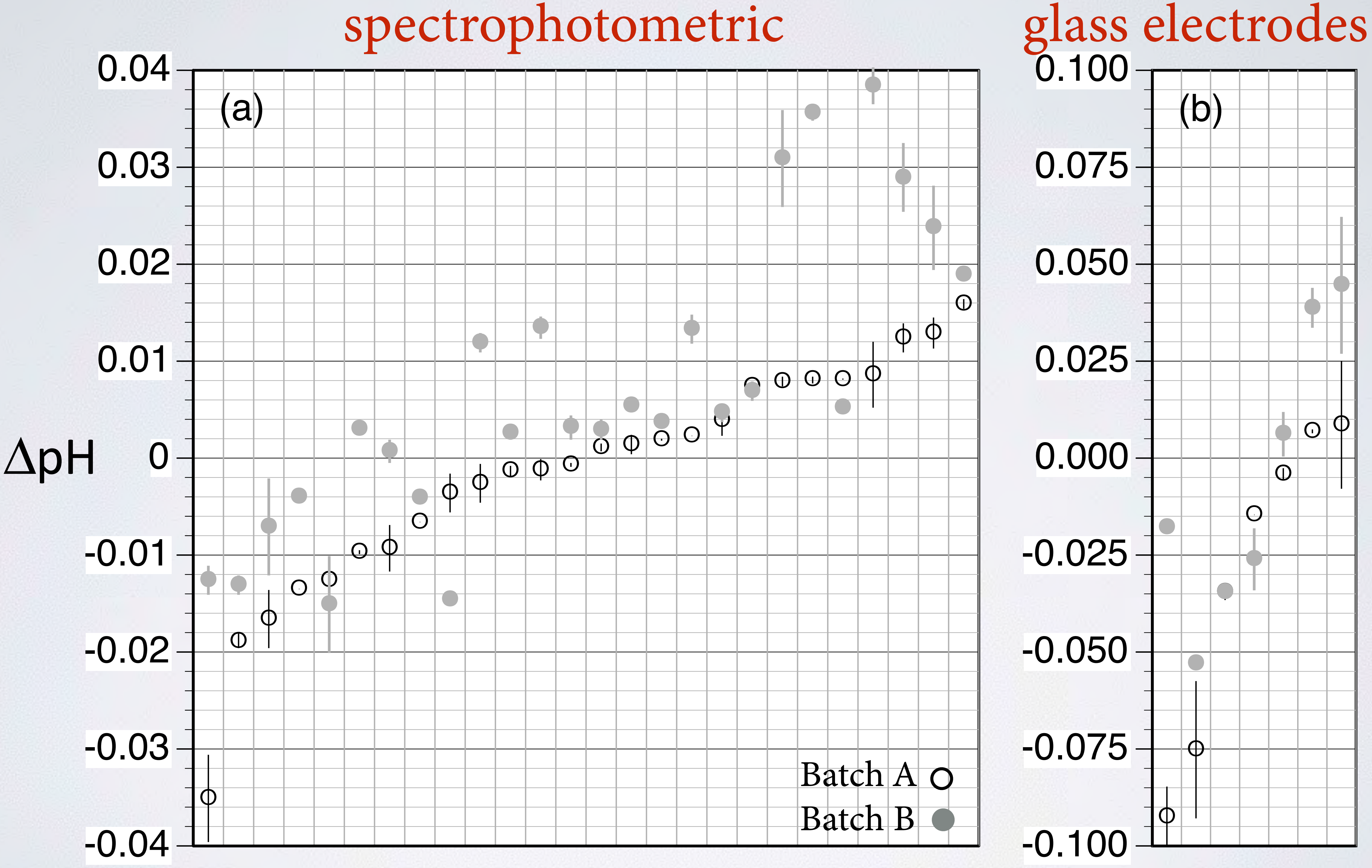

Bockmon & Dickson, 2015

FASTER, BETTER, CHEAPER

In 1992, NASA Administrator Daniel Goldin began the agency's "Faster, Better, Cheaper" initiative.

The popular consensus on "Faster, Better, Cheaper" is often expressed in the supposedly self-evident saying: "faster, better, cheaper — pick two."

Is this necessarily true for seawater carbonate system measurements?

We clearly understand the meanings of "faster" and "cheaper", but how should we define "better"?


THINK!
THERE MIGHT BE
A BETTER WAY